Refinement of the equation of state of tantalum

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The volume of tantalum versus pressure has been accurately measured up to 101 GPa by single-crystal x-ray diffraction, with helium as pressure transmitting medium. Slight deviation from previous static determinations is observed. Discrepancy with reduced shock-wave and ultrasonic data supports recent doubts about the calibration of the ruby pressure scale. Finally, first principle calculations of the literature show a positive curvature in $P(V)$ relative to the experimental data, even with a modified pressure scale.

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Ta is a transition metal (Z=73 and the Xe $4f^{14}5d^3$ $6s^2$ equilibrium atomic configuration), with a simple bcc structure stable to at least 174 GPa[1]. Because of its fundamental interest and its use as an important technology material, the equation of state (EoS) of Ta has been studied by several experimental techniques[2,3,4,1,5] and numerous ab-initio density functional theory (DFT) electronic structure calculations[6,7,8,9]. However, the EoS of Ta is still not known with a satisfactory accuracy. On the experimental side, small differences between static determinations are observed[1,5], and more important discrepancies exist among ultrasonic measurements[2], shock-wave results[3,4], and static determinations[1,5]. On the theoretical side, systematic deviations are seen between calculations with the two mostly used approximations of the exchange-correlation energy of the electrons, and reliable experimental data are needed to validate one of these approximations[9]. Here below, we report accurate EoS data of Ta, based on single-crystal x-ray diffraction (XRD), up to 101 GPa under quasi-hydrostatic conditions. We compare these data with previous measurements and DFT calculations.

Six runs were dedicated to the measurement of accurate volume data of Ta versus pressure by synchrotron single crystal x-ray diffraction, on the ID30 beamline at the ESRF (Grenoble, France). Small single crystal grains (4 μm in the maximum dimension), chosen in a tantalum powder (averaged size 10 μm, 99.9 % purity, Goodfellow product) on the basis of their external shape, were loaded in membrane diamond anvil cells, with helium as pressure transmitting medium. We checked by interferometry that the thickness of sample chamber was always larger than the dimension of the crystal. The first two experiments have been carried out using single crystal energy dispersive XRD and the other four using angle dispersive monochromatic XRD at 0.3738 Å. The same technique had been used to measure with high accuracy the equation of state of low-Z systems in the 100 GPa range[10]. An average of 7 reflections were measured in each run ; absolute uncertainty in the lattice parameter is at maximum of 10^{-3}. The pressure was estimated from the luminescence of a small ruby ball (less than 4 μm in diameter) and its quasi-hydrostatic calibration[11].

Non-hydrostatic stresses were observed to be negligible because the shape of the diffraction spot for a given reflection showed no sign of deterioration of the crystalline quality of the sample. Except in one run, when a leak of helium through a diamond fracture caused a deterioration of the pressurization conditions above 70 GPa, and the volume of a strained sample, bridged between the diamond tips, was subsequently measured.

P	V (Å³)	P	V (Å³)	P	V (Å³)	P	V (Å³)
10.9	17.142	44.2	15.204	9.2	17.243	52.5	14.814
32.0	15.717	54	14.761	10.6	17.140	58.7	14.554
41.2	15.300	35.3	15.573	12.0	17.026	65.5	14.266
11.4	17.088	52.5	14.763	13.5	16.942	70	14.143
15	16.815	71.9	14.047	15.0	16.833	90	13.449
20.6	16.473	82.5	13.697	16.1	16.751	31	15.843
25.8	16.178	84.8	13.554	17.4	16.662	36.2	15.585
31.3	15.880	85.8	13.541	19.1	16.557	39.7	15.415
36.0	15.554	91.3	13.379	20.8	16.449	45.6	15.135
41.5	15.351	95.9	13.225	22.4	16.353	50.2	14.919
47	15.069	100.9	13.145	24.0	16.263	55.5	14.693
51.4	14.853	2.3	17.838	26.2	16.129	66.5	14.257
56.8	14.566	3.6	17.704	27.9	16.036	74.1	13.998
60.8	14.453	5.0	17.585	30.1	15.914	79.9	13.795
64.3	14.42	6.7	17.436	1.1	17.933	85.8	13.634
65.7	14.307	7.8	17.354	0	18.033		

TABLE I: Atomic volume of Ta measured versus pressure by single-crystal XRD in helium pressure transmitting medium.

The $P - V$ data points measured under hydrostatic conditions are presented in Table I. They are plotted in Fig. 1 and compared to the data obtained with uniaxial stress conditions in the broken diamond run. It is seen that a non-hydrostatic pressure leads to overestimate the volume. The ambient pressure atomic volume was measured equal to 18.033(50) Å³, which agrees with ambient T and P literature data (18.065 Å³,[12]). The uncertainty in the volume determination is smaller than 3.10^{-3}, which corresponds to a pressure uncertainty of 1.5 GPa at 100 GPa. The estimated pressure error bars include the pressure gradient between the ruby ball and the Ta crystal and range from 0.05 GPa at 1 GPa to 1 GPa at 100 GPa, if the ruby pressure scale is assumed
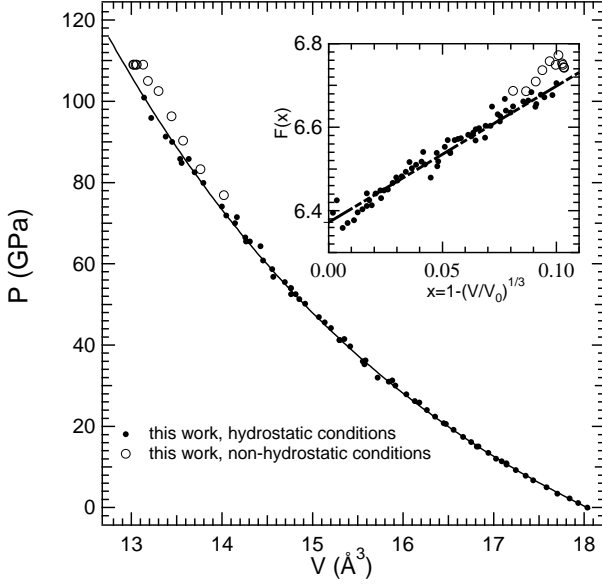
FIG. 1: Pressure versus volume data of Ta at 300K. The dots and circles are respectively the data measured under hydrostatic conditions and non-hydrostatic conditions. The full line is the Vinet fit of the data as discussed in the text. $P = 3K_0 x^{-2}(1-x)\exp(1.5(K_0'-1)(1-x))$, with $x = 1-(V/V_0)^{1/3}$ and $V_0 = 18.033$ Å^3, $K_0 = 194$ GPa, $K_0' = 3.25$. Inset : $F(x) = \ln(Px^2/(1-x)) = \ln(3K_0) + \frac{3}{2}(K_0'-1)(1-x)$, is the linearized form of the Vinet function which is used to determine $K_0' \pm 0.1$.

to be correct. Therefore, the error in the volume determination, intrinsical to the XRD technique is mainly responsible of the scattering of the experimental points as seen in Fig. 1.

To provide the useful physical parameters, namely volume V_0, bulk modulus K_0, and its pressure derivative K_0', under ambient conditions, the $P-V$ data points are generally fitted by an EoS formulation. The least square fit of the data with an universal form of the equation of state should ideally give the same value for V_0, K_0 and K_0' as the ones measured independently at zero pressure by XRD for V_0 and by ultrasound propagation for K_0 and K_0'. We have fitted the data with three most-used forms of the EoS in the literature: third-order Birch-Murnaghan EoS[13] (BM), Vinet EoS[14] (V) and the EoS proposed by Holzapfel[15] (H). In this pressure range, very similar values of K_0 (between 196 and 199 GPa), and K_0' (between 3.07 and 3.30), are obtained with these three forms, that give comparable quality of the fits. The Vinet fit has been chosen to reproduce the present data. In the case of the Vinet fit, the data can be seen in a linearized form, as shown in the inset of Fig. 1. It is seen that the data points above 50 GPa are important to unambiguously constrain the K_0' value of the slope. The results of the various Vinet fits of the data (fixing V_0, as measured; fixing V_0 and K_0 as given by ultrasonic measurements; using the recently proposed modification of the calibra-
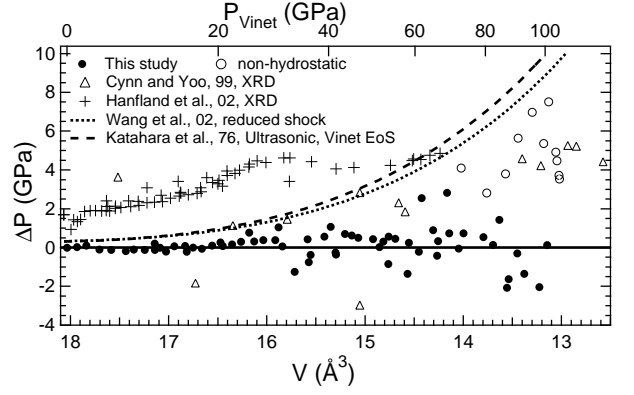

FIG. 2: Pressure difference between various experimental determination of the pressure-volume relationship of Ta. ΔP expresses the difference for a given atomic volume, between the various experimental data and our fitted Vinet EoS, and it is plotted versus the atomic volume (bottom) and the corresponding pressure given by the Vinet EoS discussed in the text.

tion of the ruby pressure scale[16]) are compared in table II to ultrasonic measurements (the adiabatic to isothermal correction had been done in ref.[2]) and to the reduced Hugoniot data[7]. The K_0 value obtained in the current study, 198 ± 3.4 GPa, is in correct agreement with the ultrasonic one, 194 GPa. On the contrary, a smaller K_0' is obtained, wether K_0 is fixed or not to its ultrasonic value.

Study	V_0	K_0	K_0'	Technique, P range, EoS
current	**18.033**	198	3.07	XRD, 0-101 GPa, V
		(3.4)	(14)	
current	**18.033**	**194**	3.25	XRD, 0-101 GPa, V
			(4)	
Cynn and Yoo[1]	18.040	195	3.4	XRD, 0-174 GPa, BM
Hanfland *et al.*[5]	18.191	207.6	2.85	XRD, 0-70 GPa, H
Katahara *et al.*[2]		194	3.83	US, 0-0.5 GPa
Wang *et al.*[4]		**194**	3.70	RSW, 0-150 GPa, V
current, mod P scale[16]	**18.033**	**194**	3.55	XRD, 0-105 GPa, V

TABLE II: Values of V_0 (in Å^3), K_0 (in GPa) and K_0' for the EoS of Ta. The current and literature X-Ray diffraction (XRD) measurements are compared to ultrasonic (US) and reduced shock-wave (RSW) measurements. For each measurement, the technique, the pressure range and the form of the EoS (V, BM, H) are indicated. The parameters that have been fixed in the fitting procedure are in bold font. Numbers between parenthesis are the fitting error bars (95 % confidence interval). The last line presents the EoS parameters obtained after modification of the pressure scale[16].

In Fig. 2, other experimental determinations of the EoS of Ta are compared through their differences with the Vinet fit of the present data (with V_0=18.033 Å^3, $K_0 = 194$ GPa, $K_0' = 3.25$). A systematic deviation between the present data and the ones of two recent XRD

measurements is clearly seen. The numerous low pressure measurements of Hanfland et al. give an atomic volume at ambient pressure of 18.186 Å^3 (0.8 % larger than the present determination). This could be due to a small contamination by hydrogen (a few percents), that is well-known to lead to an expansion of the lattice[12]. For this reason, the points plotted in Fig. 2 appear shifted from our data. Due to its larger compressibility at low pressure (Fig. 2), the values of K_0 fitted on Hanfland data cannot be reconciled with the ultrasonic value. However, the compression curve of Hanfland et al. is parallel to the current one at higher pressure. Low pressure data points measured by Cynn and Yoo[1] exhibit a large scatter. Also, an increasing deviation between the present EoS data and the data of Cynn is observed at $P > 60$ GPa. This could be ascribed to an uniaxial stress effect in Cynn experiments[17] because these data are following the trend of our data points in the non-hydrostatic run (in this study, gold has been used as an x-ray pressure standard[18] for the high pressure data points).

More severe inconsistencies exist between the present XRD and the ultrasonic measurements or the reduced shock-wave EoS of tantalum. All XRD studies lead to a smaller K_0' than the ultrasonic one. Inserting the ultrasonic values[2] of K_0 and K_0' in the Vinet formulation generates an equation of state that deviates from our determination at high pressure. As seen in Fig. 2, the EoS generated from ultrasonic values of K_0 and K_0' is in very good agreement with the EoS of Ta obtained by the reduction of shock data to ambient T[3],[4]. The difference between the XRD EoS and the reduced shock EoS or the ultrasonic based EoS reaches 12 % in pressure at 150 GPa. Possible causes of these apparent inconsistencies need to be examined and error bars estimated. The error on the reduced Hugoniot data of tantalum[4] is claimed to be of 5.5 % at 400 GPa, and less below 200 GPa. This uncertainty is caused both by uncertainties in particle and shock velocities measurements, and by the reduction procedure from Hugoniot temperature to the 300 K. The sum of the error bars in the volume determination and in the pressure measurements on the XRD EoS data points amounts to an equivalent 2.5 GPa at maximum at 100 GPa. Consequently, the consideration of cumulative error bars on the reduced Hugoniot and on the XRD EoS cannot reconcile the dynamic and static determinations of the EoS of Ta. To reconcile our XRD data with the reduced Hugoniot data and the ultrasonic based EoS of tantalum, it must be assumed that the ruby scale underestimates the pressure by about 10% at 150 GPa. A similar correction of the ruby pressure scale has been recently proposed by Holzapfel[16]. Moreover, a discrepancy between *ab-initio* calculations and x-ray measurements of the pressure-volume relation of diamond has also been ascribed to an error of the ruby pressure scale of the same magnitude[19]. As seen in table II, by using the new ruby pressure scale proposed by Holzapfel, consistency is recovered between the EoS of Ta obtained by static XRD and shock-wave measurements because similar val-
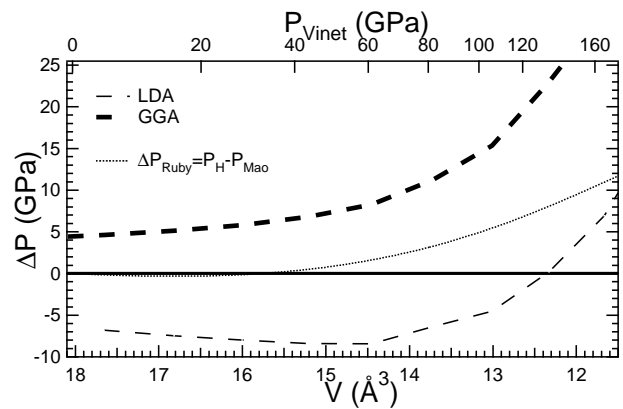

FIG. 3: Comparison between DFT calculations and experimental P-V data points at 300K. The pressure difference, for a given atomic volume, between the *ab-initio* pressure and the pressure of our fitted Vinet EoS is plotted versus volume. GGA and LDA calculations[9] are respectively represented by bold and thin lines. The pressure change due to ruby scale scale of Holzapfel[16] is indicated as dotted line

ues of K_0, and K_0' are then obtained. The ultrasonic K_0' value remains slightly (0.28) larger than the one obtained by fitting of compression data, which could be due to either experimental uncertainties or approximations in finite strain EoS formulation.

The *ab-initio* calculations of the EoS of Ta has been produced in four recent studies[6],[7],[3],[8] using density-functional theory. In principle, this method involves approximations only in the exchange and correlation energy calculation. Two forms are currently used, namely the Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA). The validity of these approximations is in practice established by their ability to reproduce experimental results. Uncertainties might also arise consequently to the choice of the computational method and of its inherent assumptions, but they should be small, as it is seen by comparing three recent GGA EoS[7],[9],[8]. These EoS agree within 3 GPa at 150 GPa, although they are based on different computational methods. Consequently, for legibility in Fig. 3, the LDA and GGA EoS are represented by the calculation of Boettger[9] alone, and they are compared to the experimental data through the pressure difference at a given volume. It is observed here, as often, that the ambient pressure volume is underestimated by LDA calculations and overestimated by GGA calculations. What seems to be more interesting here is that all DFT calculations show a similar positive curvature relative to the experimental data. The higher compressibility at high pressure of the experimental EoS compared to the DFT calculations cannot be entirely due to the possible error of the ruby pressure scale. In fact, if the new calibration proposed by Holzapfel[16], that reconciles all the experimental determinations as discussed above, is used, the larger experimental compressibility still exists, as shown

in Fig. 3, for pressures higher than 80 GPa.

In summary, the present work demonstrates that an accurate determination of the volume of metals under hydrostatic conditions in the 100 GPa range can now be achieved by synchrotron single-crystal XRD with helium as pressure transmitting medium. Consistency with the determination of the EoS of Ta by ultrasonic or shock-wave methods can be recovered by using a calibration of the ruby scale recently proposed. This highlights and estimates the present uncertainty of the ruby pressure calibration. Similar EoS measurements under good hydrostatic conditions up to the Mbar range should now be performed on reference metals to address two important issues pointed out in the present work: first, to reduce the uncertainty of the ruby pressure scale, by a comparison of these metal EoS data with the EoS deduced from high-temperature shock-wave, considered as primary standards[11]; second, to investigate if a higher experimental compressibility than the calculated DFT one is a systematic trend in metals and if it has a Z dependence.

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